Indian Journal of Chemistry
Vol.36B, May 1997, pp. 384 - 385

Rapid Communication

Application of an aluminium enolate in Mukaiyama-Michael type reaction

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Received 28 April 1997, Accepted 12 May 1997

Aluminium enolate reacts with α,β-unsaturated ketones and cinnamic esters to afford Michael adducts without the use of extra Lewis acid catalyst.

The Lewis acid catalysed Mukaiyama-Michael reaction of silyl enol ethers is one of the most important methodologies for carbon-carbon bond formations [1,2]. Although the synthetic utility of this reaction permits Michael reaction in acid medium, there still remain considerable limitations[3,4] resulting in a continued endeavour to develop milder Lewis acid catalysts[5,6]. In addition, the research for an alternate and efficient Michael donor has recently shown lithium enolates as promising substrates in asymmetric Michael reaction[7,8]. However, the generation of metal enolates usually requires either strong basic condition[9] or cleavage of silyl enol ethers by reagents such as methyllithium[10], titenium tetrachloride[11] and alkylaluminium dichloride[12]. Another disadvantage encountered in the preparation of metal enolates is the prerequisite lithium enolate mediation[13]. The aluminium reagents have attracted renewed interests and are important because of their easy accesibility and ease of handling[14]. In continuation of our interests[15] to explore the diversity of aluminium triiodide in organic synthesis, we report here a facile one-pot preparation of aluminium enolate and its first ever utility for carbon-carbon bond formation in Mukaiyama-Michael type reaction.

In Mukaiyama-Michael reaction, various lewis acids such as $TiCl_4$, $SnCl_4$, $SbCl_4$, $BiCl_3$, $ZnCl_2$, BF_3, $Sc(OTf)_3$ and salts like $TrClO_4$, $Sn(OTf)_2$ and $Bu_2Sn(OTf)_2$ are used to catalyse the reaction of silyl enol ethers to α,β-unsaturated ketones. However, in striking contrast, the use of aluminium

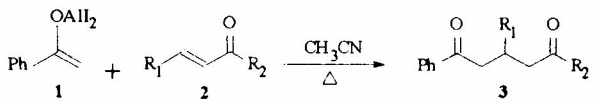

Table I — Addition of aluminium enolate to α,β-unsaturated ketones in acetonitrile

Product	R_1	R_2	m.p °C	Yield[a] (%)	Reaction period (hr)
3a	C_6H_5	C_6H_5	85	76	2
3b	*p*-Cl-C_6H_5	C_6H_5	98	70	2
3c	*p*-Me-C_6H_5	C_6H_5	92	67	3
3d	C_6H_5	OEt	60	65	2
3e	C_6H_5	OMe	94	60	2

[a] Yields are based on the starting alkenone.

enolate in Michael reactions shows certain advantages over the silyl enol ethers. In the first place,the aluminium enolate mediated Michael reaction avoided low temperature and was carried without the use of extra Lewis acid catalyst. Secondly, our strategy allowed the use of comparatively stable aluminium enolate in place of silyl enol ethers which are not always easy to prepare and are generally unstable[5d].

The aluminium enolate **1** was prepared by refluxing a solution of ω-bromoacetophenone with freshly prepared aluminium triiodide for 2 hr under an atmosphere of nitrogen. The Michael reaction was accomplished by treatment of **1** with chalcones **2a-c** in refluxing acetonitrile to afford 1,5-pentanediones **3a-c** in good yields (cf. Table I.). Similarly , the reaction of **1** with cinnamic esters **2d-e** gave 4-benzoyl-3-phenylbutanoic acid esters **3d-e** in 60-65% yields. The products were identified by spectral data and elemental analyses. In all the above reactions acetophenone was isolated as a minor product (8-10%) resulting from the hydrolysis of enolate **1**.

In conclusion we have shown that the aluminium enolate **1** provides a novel route for carbon-carbon bond formation in Mukaiyama-Michael reaction. Our procedure will widen the scope of the Mukaiyama-Michael reaction as aluminium enolates are stable and could be conveniently employed as Michael donor. Further work on aluminium enolates are in progress and will be reported in due course.

Experimental Section

Preparation of 1,3,5-triphenyl-1,5-pentadione 3a: General procedure. ω-Bromoacetophenone (0.2g, 1 mmole) and freshly prepared aluminium triiodide (1 mmole) were refluxed in dry acetonitrile (25 mL) under an atmosphere of nitrogen for 2 hr. The solvent was removed under reduced pressure to obtain an orange solid product of the enolate **1** which was stored carefully under nitrogen atmosphere. A solution of chalcone **2a** (0.80 mmole) in acetonitrile (10 mL) was added to it under anaerobic condition and the mixture refluxed for 2 hr. On completion of reaction, the reaction mixture was hydrolysed by addition of water (50 mL) and extracted with ethyl acetate (3×25 mL). The organic extract was washed with aqueous sodium thiosulphite solution (5%) and dried. Removal of the solvent afforded 1,3,5-triphenyl-1,5-pentane-dione **3a** and acetophenone respectively in 76% and 8% yields. The reaction of aluminium enolate **1** with **2b-e** similarly yielded **3b-e** in 60-70% yields.

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